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A hexagonal crystal with star-shaped core, a novel crystal morphology never seen before, was found in low molecular weight poly(L-lactide) (LMw-PLLA) modified by glycine ester based ionic liquid. The increase in polymer chain mobility, caused by the ionic liquid dilution and interaction with polymer chains, induces a morphology transformation from hexagon-shaped ring-banded spherulites to non-banded polymer chains, without a dendritic pattern. The ionic liquid induced lamellar assembly leading to a novel crystalline morphology never seen before in PLLA either in melt-crystallization or solution grown process. Some studies reported that the single crystals can grow to form mature crystal which has similar single crystal shape. In this study, the novel crystals of PLLA/PBA (70/30) blend. Furthermore, the ring-band spacing was reported to decrease by increasing the amorphous polymer content. The original morphology of neat PLLA was disrupted as the amorphous PDLLA content increased. The amorphous PDLLA appeared as dark spots in polarized optical microscopy observation. A recent study in our lab has reported the formation of multiple spherulites patterns in the blend of LMw-PLLA and 30 wt.% poly(p-vinyl phenol) (PVP). After the addition of PVPh into PLLA, not only the PLLA spherulite pattern changed, but also the number of spherulite pattern diversified. In general, many studies reported that the crystalline morphology of PLLA might change upon the addition of another interacting component/diluent. However, the influence of ionic liquids on the PLLA morphology has rarely or never been reported. Ionic liquids, with multiple functional groups and ionic bonding in their molecular structures, are potentially capable of interacting with polyesters such as PLLA.

Room-temperature ionic liquids have many characteristics, such as: high ionic conductivity; high chemical and thermal stability, low melting points, low vapour pressure (non-volatile), non-flammable, and potential of broad applications. With their excellent properties, the ionic liquids (ILs) may be considered for applications such as solvents, reagents, catalysts, and as materials themselves. IL’s have been reported as green plasticizers for some petro-based polymers such as poly(vinyl chloride) (PVC) and poly(methyl methacrylate) (PMMA). In this study, we introduced a glycine ester based ionic liquid, which consists of N-alkyl-substituted glycine ester [Gly]+ and bis(trifluoromethanesulfon)yl]imide [TFSI]−, into PLLA. For information, the chemical structure of the ionic liquid is shown in Scheme 1 (supporting information). This study was focused on the morphological changes as ionic liquid incorporation was introduced into biodegradable PLLA. The ionic liquid induced lamellar assembly leading to a novel crystalline morphology in PLLA/IL was also observed and analyzed. This novel morphology has never been observed in melt-crystallized and solution grown samples of either neat PLLA or PLLA blends. The crystal growth mechanism was analyzed and the presence and effect of the ionic liquid on the crystallized morphology of PLLA were proposed.
morphology can be compared to the single-crystal like crystals observed in poly(ethylene succinate) (PESu) diluted with interacting amorphous polymers. A recent study in our lab.\(^1\) has reported that the polymer single crystals may grow to form a crystal pattern that resembles the shape of its single crystal. In that study, lozenge-shaped single crystals of poly(ethylene succinate) (PESu), when blended with poly(p-vinyl phenol) (PVPh) and melt-crystallized in thin films, grow and stack to form a dendritic morphology.\(^1\) The shape of the dendritic morphology resembles monolayer PESu lozenge single crystals. Effects of ionic liquid for PLLA may be similar to that of PVPh to PESu on crystal formations approaching single-crystal-like assembly upon melt-crystallization. The addition of a small amount of ionic liquid (5 wt.\%) into PLLA induces the formation of different PLLA crystal morphology. It shows non-birefringent hexagonal crystal which has a hexagon star-shaped central core. The hexagon-shaped central core in neat PLLA crystal becomes the star-shaped central core after the addition of ionic liquid. This composite crystal (large hexa-stalks with a small star-shape core) seems to grow in two steps. The observation of crystal growth will be discussed in the next section.

![Fig. 1 Polarized optical microscopy (POM) and optical microscopy (OM) images of crystalline morphology of neat PLLA (a) and PLLA/IL (95/5) (b).](image)

Fig. 2 shows the AFM height image, phase images, and height profiles of the hexagonal crystal in PLLA/IL (95/5), melt-crystallized at \(T_c = 110\)°C. The AFM height image in Fig. 2 displays the overall morphology of the crystal. Apparently, there are three distinct regions, which are star-shaped central core, straight long stalk-crystals growing from the six corners of the central core, and outer central core regions, indicated by red square 1, 2, 3, respectively, as representative cases. The lamellar pattern in those three regions is similar, that is composed of aggregated spherical flat-on lamellae packed like fish-scales. The difference between those three regions is mainly the thickness. The AFM height profiles show that the central core region is much higher than the outer central core region. The height of the central core region is about 850-900 nm, as shown by red dashed line in Fig. 2. Region 2 (straight thick stalks growing from the six corners of the central core) is slightly higher than the outer central core region. The height of region 2 is above 200 nm, as shown by white dashed line in Fig. 2.

In-situ monitoring of novel crystal formation can be helpful in investigating the formation progress of star-shaped central core from hexagon-shaped to star-shaped and final crystal pattern. Fig. 3 shows a series of time in-situ OM images exhibiting the development of crystals (a) and the growth rate of crystal melt-crystallized at \(T_c = 110\)°C (b). The first OM image in Fig. 3a was captured 2 min after the sample was quenched to \(T_c\) from a molten state. The small crystal appeared as hexagon-shaped crystal, which is the core to be surrounded by later-grown crystals. This hexagon-shaped crystal then continued to grow until 20 s after first photo-capturing (2 min). After 30 s from first photo-capturing, the hexagon-shaped crystal stopped growing (or slowly grew) and transformed to form star-shape crystals, and the surrounding/outer region appeared simultaneously. The outer region then continued to grow and some straight thick stalks simultaneously appeared from six corners of the star-shaped central core. The final crystal pattern was composite hexagon-shaped crystal with a star-shaped core. The star-shaped crystal became the central core for the big hexagonal-shaped crystal, leading to the formation of a hexagon-in-hexagon composite crystal morphology. The growth rate of the central core and outer region were found to be different. The growth rate of the central core was faster than that of the outer region. Hence, this crystal is suggested to grow with two steps growth rate. The faster growth rate of the central core region caused the lamellae aggregates, eventually the much thicker central core was formed. The relation between ionic liquid addition into PLLA with two-steps growth in the crystal formation will be discussed later. Fig. 3b shows the change of spherulite radius relative to time. The radius of the spherulite shows linear change with time, and slope of the graph can be measured as the crystal growth rate. The rate of the first-step growth is 0.549 \(\mu\)m/s and the second-step is 0.397\(\mu\)m/s.
To further understand the mechanism of composite hexagon-hexagon-core crystal formation, Fig. 4 shows a scheme to illustrate the crystal formation during melt-crystallization process. Firstly, the nucleus grew to form hexagon-shaped small crystal as the initial core. As already mentioned previously that the lamellae of polymer could grow to form patterns which resemble the shape of polymer single crystal. The lamellae in early stage grew fast, as confirmed by the measured growth rate in Fig. 3b. Moreover, the nucleation rate increased with the addition of ionic liquid. In this present study, $T_c$ of PLLA decreased after the addition of ionic liquid. Fig. S1 (supporting information) shows the DSC thermograms of PLLA and PLLA/IL (95/5). The $T_c$ of the blend shifts to a lower temperature, indicating higher polymer chain mobility that facilitates the nucleation process. Then, the hexagon-shaped small crystal grew rapidly until the certain time at which the crystal could not grow as fast as the stage of post-nucleation. The area at which no lamellae can grow is indicated as the depletion zone. Abundant crystallizable materials crystallized in a short time might cause the depletion zone during the crystal growth. Height profile in Fig. 2a shows that the depletion zone appears after the core and before the outer central core regions. After the depletion zone appeared, the crystallizable materials started to continue growing in the area of core surrounding. Simultaneously, since the crystallizable materials were more limited in the central core region and the corners of central core grew faster than edges of central core, so the hexagon-shaped central core only slightly grew in the corner of hexagonal shape. Consequently, the edges of the hexagon-shaped crystal were pushed inside, leading to the formation of star-shaped central core as shown in Fig. 4a- (ii) and (iii). The increase in polymer chain mobility, enhanced by the ionic liquid addition, facilitates a morphology transformation from hexagon-shaped to six-arm star-shaped morphology. After the star-shaped central core formation, the remaining crystallizable materials in the core continued to grow to form straight thick stalks which are parallel to the six corners of the central core. Those stalks grew together with outer core region, as shown in Fig. 4a(iv). Then, the crystal continuously grew to form bigger and more mature crystal. The addition of the ionic liquid induced a dilution effect to the PLLA growth. Fig. S2 shows the growth rate of neat PLLA at the same $T_c = 110 \degree C$. By comparing Fig. 3b and Fig. S2, the neat PLLA has a faster growth rate than the latter-step crystal growth in PLLA/IL (95/5) blend.

The ionic liquid in the blend was rejected or excluded to the growth front from PLLA-rich domain during crystallization. Fig. 4b displays the mechanism of crystal formation from melt-crystallization. In the molten state, the ionic liquid is mixed with amorphous region (amorphous portion and molten crystalline portion of PLLA). In the crystallized state, the PLLA crystals appear and the amorphous portion of PLLA remains to mix with the ionic liquid, which both are rejected to the growth fronts of PLLA crystals in horizontal and vertical directions. To confirm the ionic liquid existence in rejected regions of the crystallized state of the mixtures, the sample was water-etched. The crystal surface roughness of the etched sample was then characterized using AFM. The cation end of the ionic liquid is ester-based compound, so the ionic liquid can be soluble in water. Fig. S3 shows the AFM images of the blend sample before and after water-etching. The height profiles display that the crystal surface before etching is smoother than that after etching. It means that the rougher crystal surface is caused by the removal of ionic liquid from the rejected region in crystallized state of the mixture, as...
illustrated in Fig. 4b. This observation confirms that the ionic liquid, together with the amorphous part of PLLA, are rejected or excluded to the growth front during crystallization.

Conclusions

In summary, formation of a novel composite star-shape core-in-hexagon morphology in PLLA has been discovered. By blending with a glycine-ester based ionic liquid, a composite hexagon-stalk crystal with six-arm star-shaped central core was formed. Mechanisms of such unusual morphology (hexagon superimposed on a star-shape core) were probed in depth. The higher polymer chain mobility, caused by the ionic liquid dilution and interaction with PLLA polymer chains, induces a dramatic morphology transformation from hexagon-shaped ring-banded spherulites to a composite pattern of non-banded hexagon with star-shaped core. This crystal pattern of the hexagons-with-star-core spherulites is composed by aggregated spherical flat-on lamellae preferentially oriented in six equally divided directions from the nucleus center. The incorporation of ionic liquid into PLLA induces two steps crystal growth rate, leading to the formation of hexagon crystal with central core. Subsequently, the higher polymer chain mobility in the blend, enhanced by ionic liquid addition, leads to the transformation from hexagon-core to star-core. The two-step growth leads to the composite crystals with a unique pattern as observed. The results in this Communication show that a properly chosen ionic liquid could be used to control the crystal morphology of PLLA. Furthermore, analyse on this system revealed basic understanding why there were such intriguing morphologies, based on interactions and kinetics driving forces between PLLA and IL.

Notes and references

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A novel hexagonal crystal with star-shaped core is found in LMA-PLLA blended with an ionic liquid and melt-crystallized at Tc = 110°C.